

UNCLASSIFIED

AD NUMBER

**AD484216**

NEW LIMITATION CHANGE

TO

**Approved for public release, distribution  
unlimited**

FROM

**Distribution authorized to U.S. Gov't.  
agencies and their contractors; Critical  
Technology; MAY 1966. Other requests shall  
be referred to Air Force Aero Propulsion  
Laboratory, Wright-Patterson AFB, OH  
45433.**

AUTHORITY

**AFAPL ltr, 12 Apr 1972**

THIS PAGE IS UNCLASSIFIED

484216

ELECTRODE PASSIVATION STUDIES

Contract No. AF 33(515)-3433

Second Quarterly Report  
Covering Period March 1,  
Through May 31, 1966

For  
Department of the Air Force  
Air Force Aero-Propulsion  
Laboratory  
Wright-Patterson Air Force Base  
Ohio

This report was prepared by S. B. Brummer, A. C. Makrides, and J. Bradspies. Mr. R. Marsh is technical monitor of the work performed under this contract.

The work covered by this report was accomplished under Air Force Contract AF 33(615)-2433, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

Notice:

Foreign announcement and distribution of this report is not authorized. Release to the clearinghouse for Federal Scientific and Technical Information, CFSTI (formerly OTS) is not authorized. The distribution of this report is limited because it contains technology identifiable with items on the Strategic Embargo Lists excluded from export or re-export under U. S. Export Control Act of 1949 (63STAT. 7), as amended (50 USC APP 2020, 2031), as implemented by AFR 400-10.

## CONTENTS

<b>Abstract</b>	<b>iv</b>
<b>I. Introduction</b>	<b>1</b>
<b>II. Work Completed Under Contract</b>	<b>2</b>
A. Zinc and its Alloys	2
B. Corrosion of Mg	11
<b>III. Conclusions</b>	<b>14</b>
<b>IV. Future Work</b>	<b>15</b>

## FIGURE CAPTIONS

### Figure No.

- 1 Corrosion of Zn in KOH
- 2 Anodic Dissolution of Mg in 1N KOH at 30°C, unstirred
- 3 Anodic Dissolution of Cu in 1N KOH at 30°C, unstirred
- 4 Anodic Dissolution of Cu in 6N KOH at 30°C, unstirred
- 5 Anodic Dissolution of Ti in 1N KOH at 30°C, unstirred
- 6 Anodic Dissolution of Mn in 1N KOH at 30°C, unstirred
- 7 Corrosion of Zn and 97 Zn - 3 Mg in N KOH at 30°C
- 8 Anodic Dissolution of 97 Zn - 3 Mg in 6N KOH at 30°C, unstirred
- 9 Anodic Dissolution of 97 Zn - 3 Mg in 6N KOH at 30°C, unstirred
- 10 Anodic Dissolution of 67 Cu - 33 Zn in 1N KOH at 30°C, unstirred
- 11 Anodic Dissolution of 80 Zn - 20 Cu in 1N KOH at 30°C, unstirred
- 12 Anodic Dissolution of Mg at 30°C. (a) 1N  $\text{NaClO}_4$  buffered to pH 7 with  $\text{NaH}_2\text{PO}_4$ ; (b) 1N  $\text{NaClO}_4$  unbuffered; (c) 0.2M NaF at pH 2 (using HF).

## ABSTRACT

Studies of the passivation of Zn and Zn-alloys in KOH at 30°C have been made potentiostatically. Zinc shows the characteristic active-passive current-potential curve although the passive current is too high for use in the passive reserve mode in Zn-AgO batteries. Studies of the corrosion of Co, Cu, Fe, Mg, Mn, and Ti in alkaline solutions show them as possible choices for alloying with Zn to improve its standby characteristics. Cu-Zn alloys are not acceptable, however, since the addition of Cu lowers the Zn critical current but does not lower the passive current sufficiently. Zn-Mg solid solutions show the formation of an inactive surface layer and are therefore not suitable. Cu-plating of Zn may be suitable for its protection on standby.

Studies of the passivation of Mg from pH 2 to 14 were carried out with a view toward using the high energy density characteristics of the Mg-m-dinitrobenzene battery. In neutral and alkaline solutions Mg is passive on open circuit and cannot be used in the passive reserve mode. A secondary passivation may be present in mildly acid fluoride solutions.

## I. INTRODUCTION

During this quarter we have concentrated our studies on the Zn and Mg anodes. Dissolution and passivation of Zn and its alloys have been investigated in alkaline solutions with particular reference to the use of the zinc-silver battery as a passive reserve system. Mg has been investigated with a view toward using the Mg-m-dinitrobenzene (m-DNB) system in acid solutions.

With respect to the Zn system, we have investigated the active-passive transition of zinc and its alloys in 1N and 6N KOH. The 1N alkali is less aggressive than the normal battery electrolyte and allows us to establish whether a given system has sufficient promise to merit attempted exploitation either by changing the alloy composition or by modifying the electrolyte. (An example would be adding neutral salt to increase conductivity while controlling the corrosion resistance by not changing the pH.) The 6N KOH better simulates the battery electrolyte as it is presently constituted. Corrosion resistance to these electrolytes of a number of elements which might be suitable for alloying with zinc has been examined and where appropriate the behavior of alloys has been investigated.

The corrosion behavior of pure Mg in a number of different electrolytes in the range of pH from 2-14 has been investigated with a view toward discovering whether its normal dissolution is trans-passive. If so, the simple concept of passive storage is not feasible.

## II. WORK COMPLETED UNDER CONTRACT

### A. Zinc and its Alloys

The behavior of zinc and its alloys in alkaline solutions has been investigated with a view toward using the zinc-silver battery in the passive reserve mode.

#### 1. Factors Governing Selection of Alloying Elements

The factors governing the choice of suitable elements for alloying with Zn have been considered in some detail in this period. One important factor governing the selection must be that the alloying element is as non-noble as possible so that it will not raise the potential of the anode and reduce the power density of the battery. Information about this is readily available (Latimer, Oxidation Potentials (1952) or Pourbaix, Atlas of Electrochemical Equilibria (1965)) although in very alkaline solutions it is of dubious reliability. Another important characteristic of the alloying constituent then must be the ability to form a passive layer in a potential region below the  $\text{AgO}/\text{Ag}_2\text{O}$  potential ( $\sim 1.35$  v vs. R. H. E.). This passive layer must be readily removable for activating the battery. Accurate information about these aspects, i. e. the actual kinetic behavior of elements in alkaline solutions, is scarce and even less reliable than the theoretical (thermodynamic) information mentioned above. On the basis of thermodynamic considerations and on general electrochemical corrosion grounds, we might attempt to alloy with V, Ti, Zr, Hf, Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Cd, In, and Mg. However, alloying Zn with Ti, Zr, Hf, V, Nb, Ta, Cr, and In is either very difficult or impossible. This leaves Mn, Fe, Co, Ni, Cu, Cd, and Mg as reasonable possibilities. Some of these elements are more noble than zinc itself, and this may turn out to be a problem.

## 2. Experimental

The experimental arrangement for the study of the current potential curves involves the typical three-electrode system (working, counter, and reference) in a Pyrex cell. The working and counter-electrode compartments are blanketed in "pre-purified"  $N_2$ . In the reference compartment we use "tagged"  $H_2$  to fix the potential of our  $Pt/H_2$  reference system. We avoided the use of a calomel reference electrode because of the danger of contamination with  $Cl^-$ , a well known passive film destroyer. Potentials are given against the reversible hydrogen electrode in the working solution (R. H. E.). The working electrode is usually a polished cylinder ( $\sim 1 \text{ cm}^2$  area) which is tapped, threaded, and mounted on a Teflon gasket. Some alloys are too brittle to be threaded, and are, therefore, soldered to a Pt wire sealed through soft glass. The Pt and Pt-alloy contacts were covered with melted Kel-F or with irradiated polyolefin. Experiments were carried out at  $30 \pm 0.2^\circ\text{C}$  in KOH or in other electrolytes as indicated.

It was decided to do most of the experiments without stirring in KOH containing no zincate since these conditions best simulate the conditions in a primary battery. The absence of stirring is obvious (zinc dissolution is sensitive to stirring), but the absence of zincate perhaps requires some explanation. In a secondary battery the zincate aids recharge and also lessens corrosion on standby. Neither of these is relevant in a primary battery, particularly a reserve battery.

Where appropriate, the potential was stepped (via an electronic potentiostat) so as to evolve  $H_2$  in between each point. During this treatment any passive films formed previously tend to be reduced. Also, the solution is vigorously stirred for one minute to carry previously dissolved zincate into the bulk of the solution. The stirring is discontinued for one minute to allow the solution to become quiescent and then the potential of the electrode is raised to the next

potential of interest. This procedure is to obtain reproducible and appropriate surface and solution conditions. It is not valuable for some materials since passive film reduction is sluggish. At the potential of interest, we record the current as a function of time and observe any changes in the appearance of the electrode. When the current is steady (after  $\sim$  60 seconds over most of the potential region of interest for zinc itself, but observed for at least another 5 min), we revert back to the  $H_2^-$  evolution potential ( $\sim$  - 0.8 to 1.0 v vs. R. H. E.) in preparation for the next point. In this way we are able to obtain currents at a fixed potential which reproduce from sample to sample and during the course of an extended experiment, to within 10% for Zn.

### 3. Corrosion of Zinc

Typical current-potential curves for Zn in unstirred 1N and 6N KOH at 30°C are shown in Fig. 1. The curves show the characteristic active-passive transition with increasing potential above about - 0.1 v vs. R. H. E. The currents were stable with time in the active dissolution region (less than 10% change from 1 - 10 min at each potential) but less so in some parts of the passive region. For example, in 1N KOH, at +0.1 v,  $i_{1 \text{ min}}$  was 3.9 mA and  $i_{7 \text{ min}}$  was 3.7 mA. The electrode was white under these conditions (probably  $Zn(OH)_2$ ). Similarly at 0.6 v, where the electrode becomes brown,  $i_{1 \text{ min}}$  was 6.0 mA,  $i_{7 \text{ min}}$  was 5.5 mA and  $i_{45 \text{ min}}$  was 4.5 mA. The largest change with time is seen in the transition region between the active and the passive regions (- 0.35 to - 0.1 v). For example at - 0.1 v,  $i_{1 \text{ min}}$  was 7 mA and  $i_{10 \text{ min}}$  was 3.7 mA. The variation with time in 6N KOH, where the dissolution rate is much higher, was even less. The colors which the electrode took under the various conditions of polarization are also indicated on the graph.

As indicated, these curves show that Zn in KOH has the characteristic active-passive dissolution curve and the one required

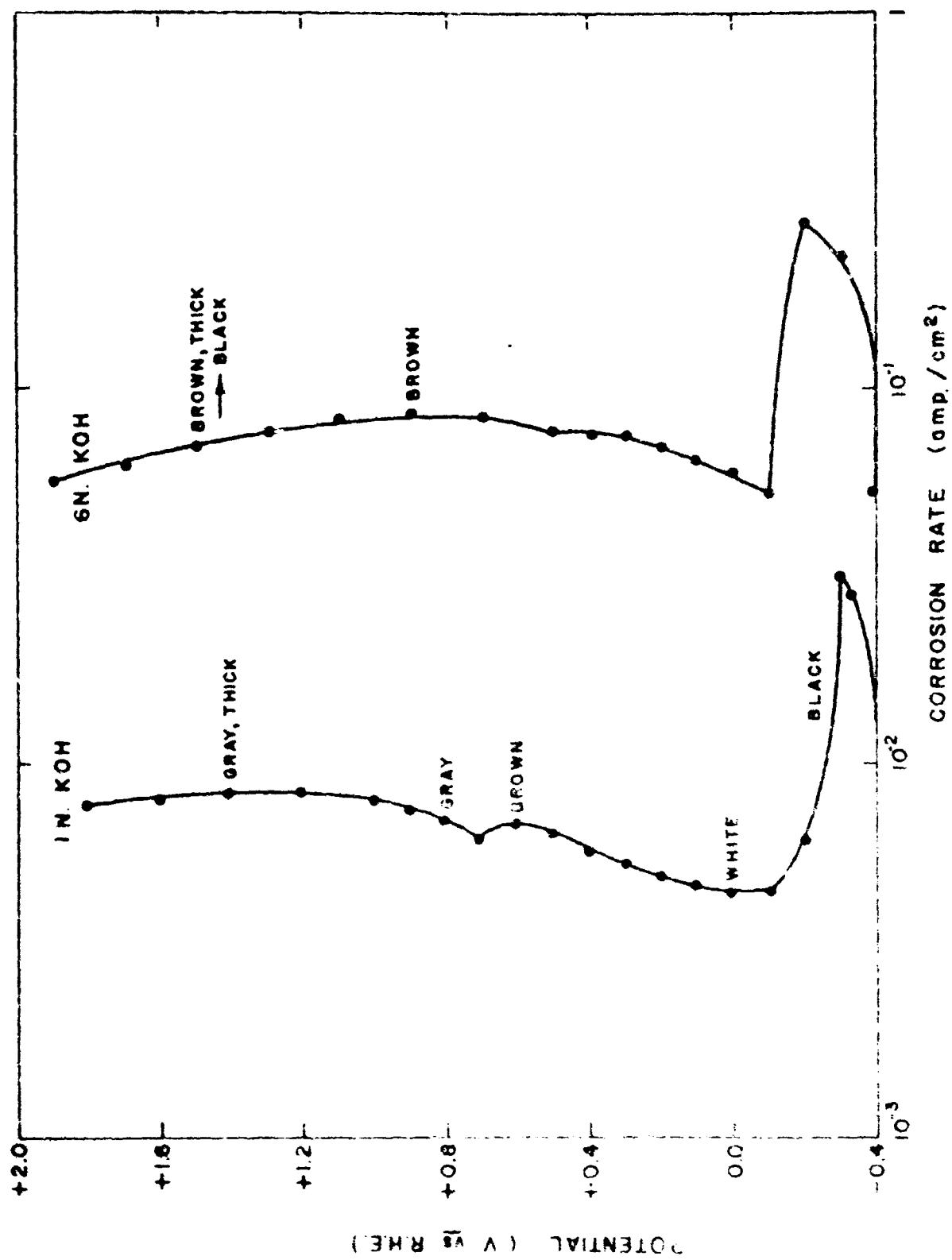


Fig. 1 Corrosion of Zn in KOH

for the present purpose. However, while the active dissolution rate is suitably high, the passive dissolution rate is much too high ( $\sim 4.5 \text{ mA/cm}^2$  in 1N KOH and  $55 \text{ mA/cm}^2$  in 6N KOH under the best conditions). An appropriate passive dissolution rate is perhaps one microampere per  $\text{cm}^2$ . To achieve this, one can alloy the zinc (either as a solid solution or as in an intermetallic compound) with an element which passivates better in KOH but which still dissolves readily at the anode potential of the Zn-AgO battery.

#### 4. Tests of Possible Alloying Elements

Corrosion tests on a number of elements were carried out in KOH to test appropriateness for alloying with Zn.

The current potential curve for Mg in 1N KOH is shown in Fig. 2. This metal approaches the desired passive current but is not readily activated; indeed, we have not really found any significant potential region of active dissolution.

The corrosion of Cu was investigated in 1N and 6N KOH (Figs. 3 and 4). In 1N KOH, Cu shows a typical active-passive transition, being active at  $\sim 0.8 \text{ v vs. R.H.E.}$  and showing a minimum of passive current at 1.1 v. The currents depended very strongly on time. For example, after 45 minutes at 1.0 v, the corrosion rate was  $0.6 \mu\text{A/cm}^2$  and the electrode was covered with a dull brown film.

Activation was readily achieved with a cathodic galvanostatic pulse, and a number of potential arrests were seen before  $\text{H}_2$ -evolution. The charges involved in these potential arrests were dependent on the current density, suggesting the reduction of solution species rather than (or in addition to) surface oxides. Under some circumstances the electrode acquired black, veiny films which could not be reduced galvanostatically.

Figure 2

Anodic Dissolution of Mg in 1N KOH at 30°C, unstirred

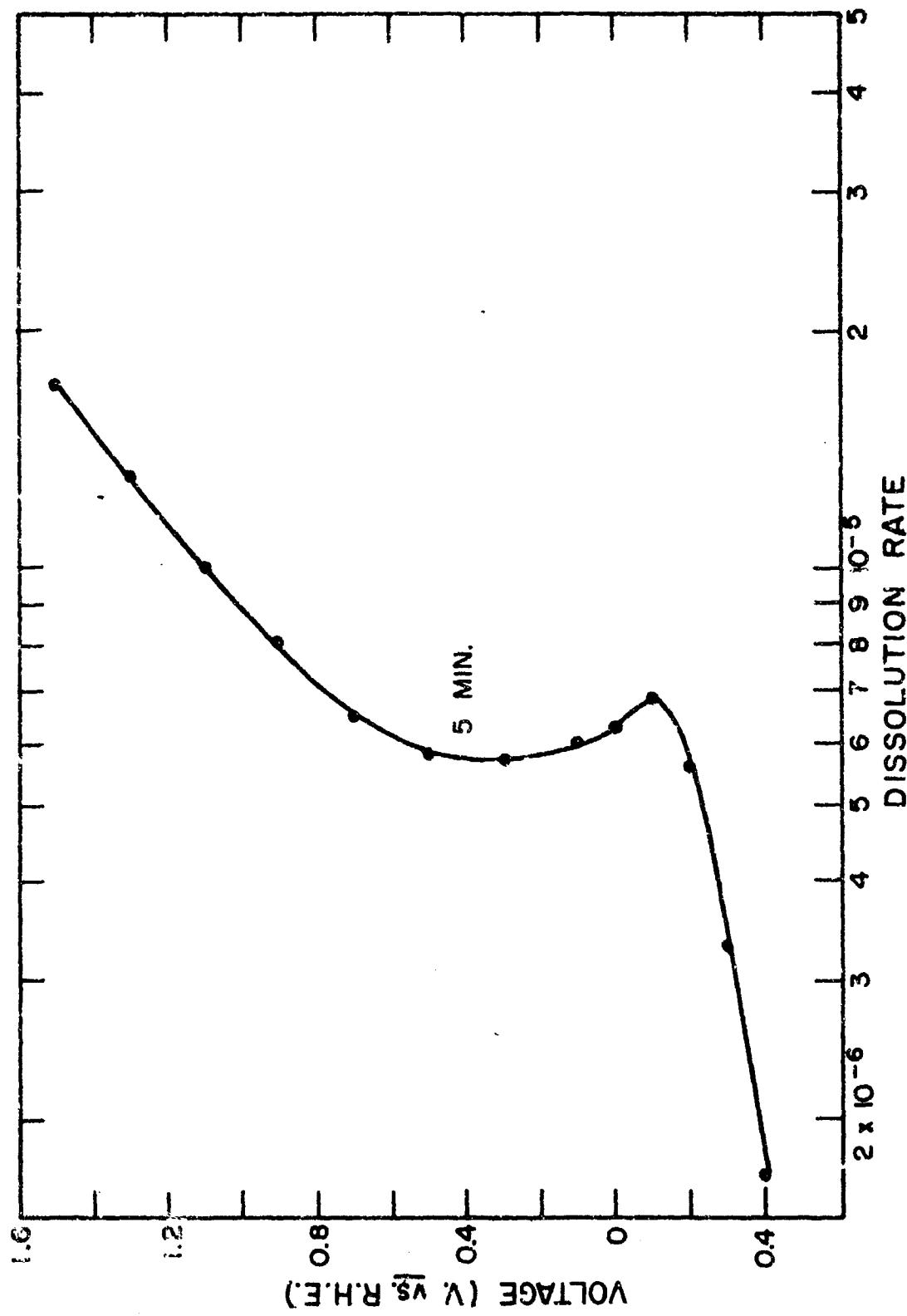


Figure 3

Anodic Dissolution of Cu in 1 N KOH at 30°C, unstirred

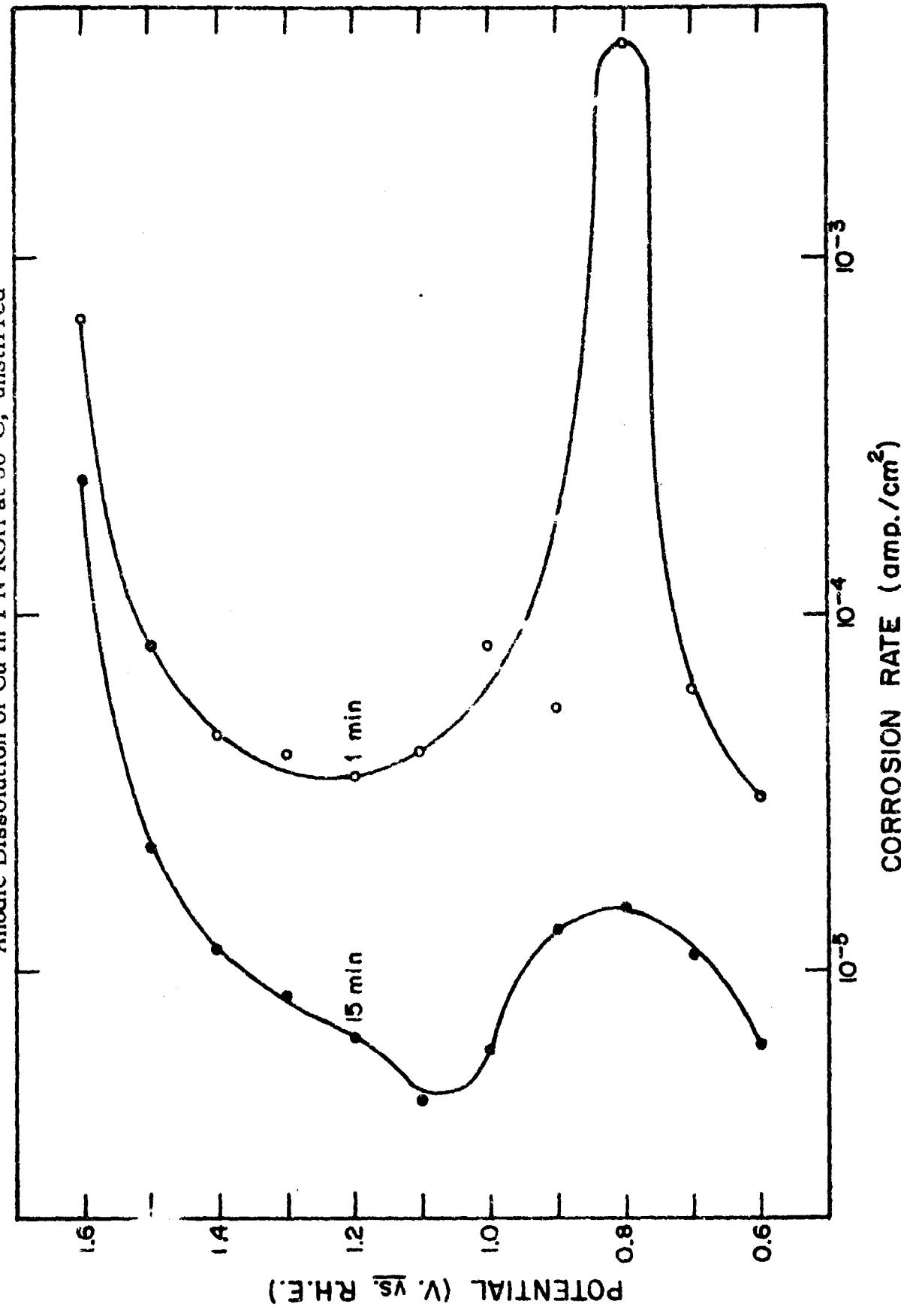
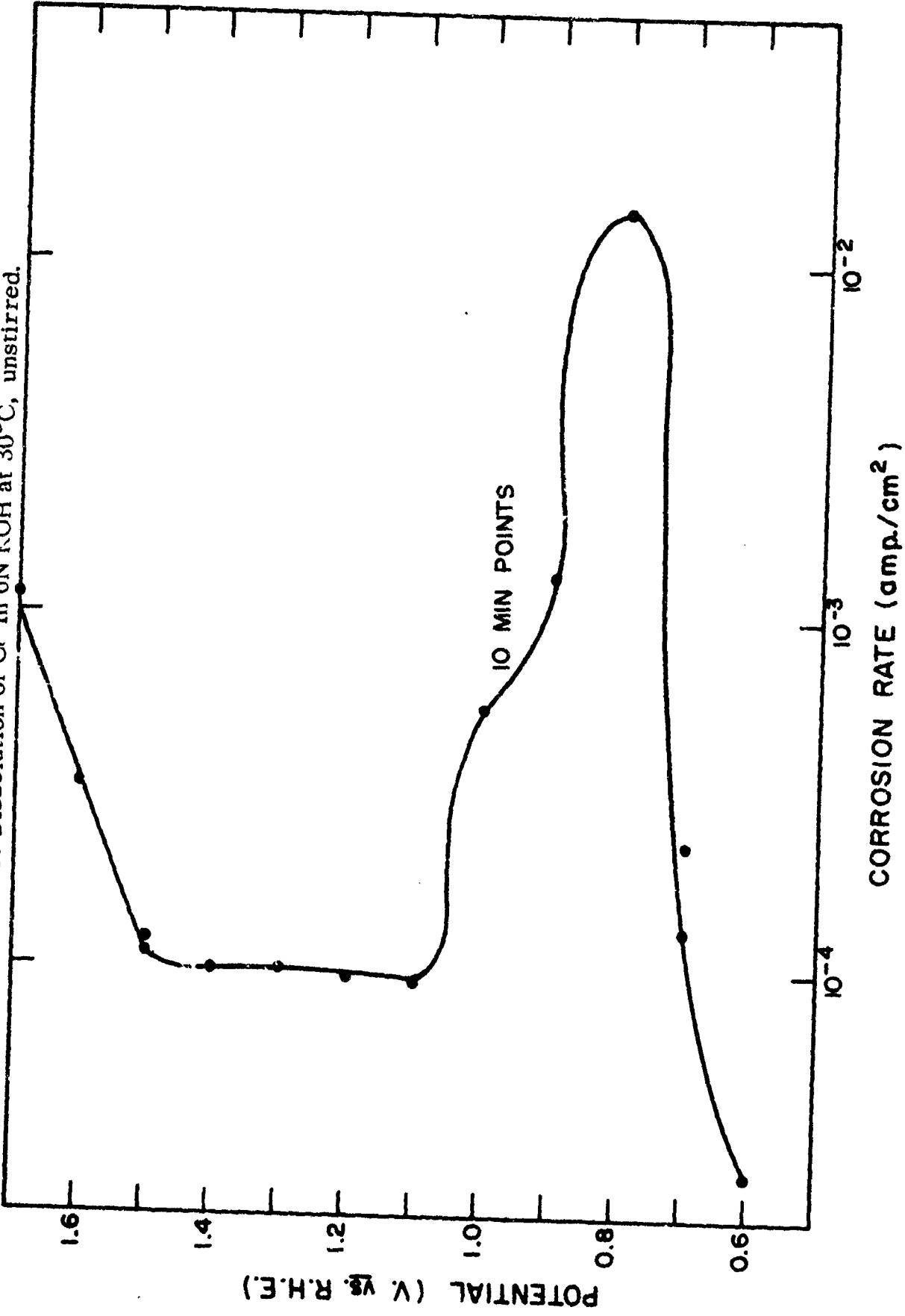


Figure 4  
Anodic Dissolution of Cr in 6N KOH at 30°C, unstirred.



In 6N KOH (Fig. 4) the currents were much steadier, but the dissolution rate was considerably higher. For example, the passive current was  $10^{-4}$  amp/cm<sup>2</sup>. Again, the electrode went through various color stages in different potential regions. The greater corrosion rate of Cu in 6N KOH is related to complexing of Cu(OH)<sub>2</sub> by KOH; for example, we found that Cu(OH)<sub>2</sub> is relatively insoluble in 1N KOH and soluble in 6N KOH.

It was thought inappropriate at this juncture to investigate the corrosion of Cu in greater detail. It is clear from Fig. 5 that Cu does have suitable corrosion characteristics in 1N KOH for our purposes.

The corrosion of Ti in 1N KOH is of the right order for the present purpose (Fig. 5) although the active dissolution region is so low that activation after standby passivation would be difficult. The passive current is fairly low and, for example, after one hour at 1.0 v falls to about 2.5  $\mu$ A/cm<sup>2</sup>. After being taken to 1.6 v in an extended run, the Ti looks little different from its original condition but reduction of what is certainly a passivating film is very difficult since there are no potential arrests at - 1 mA/cm<sup>2</sup> before H<sub>2</sub>-evolution. In 6N KOH, Ti tarnished after a short while at potentials above the hydrogen potential. Currents were unsteady but low enough to suggest the possible usefulness of Ti in this medium (a few  $\mu$ A/cm<sup>2</sup> after several minutes at 1.0 v). One of the problems with the Ti system is that although compounds with Zn have been reported (Hansen, Constitution of Binary Alloys), they are apparently very difficult to make. We are investigating this.

The corrosion of Mn in KOH has also been investigated. Corrosion currents were low. (Fig. 6 shows 5 min. points) and rather unsteady, declining rapidly with time. For example, in one experiment at 0.8 v, the current fell from 150 to 50  $\mu$ A/cm<sup>2</sup> going from 1 to 5 min; at 1.4 v it fell a similar factor in this time range. On reduction from high potentials (e.g. 1.4 v) there was a long

Fig. 5 Anodic dissolution of Ti in 1N KOH at 30°C, unstirred

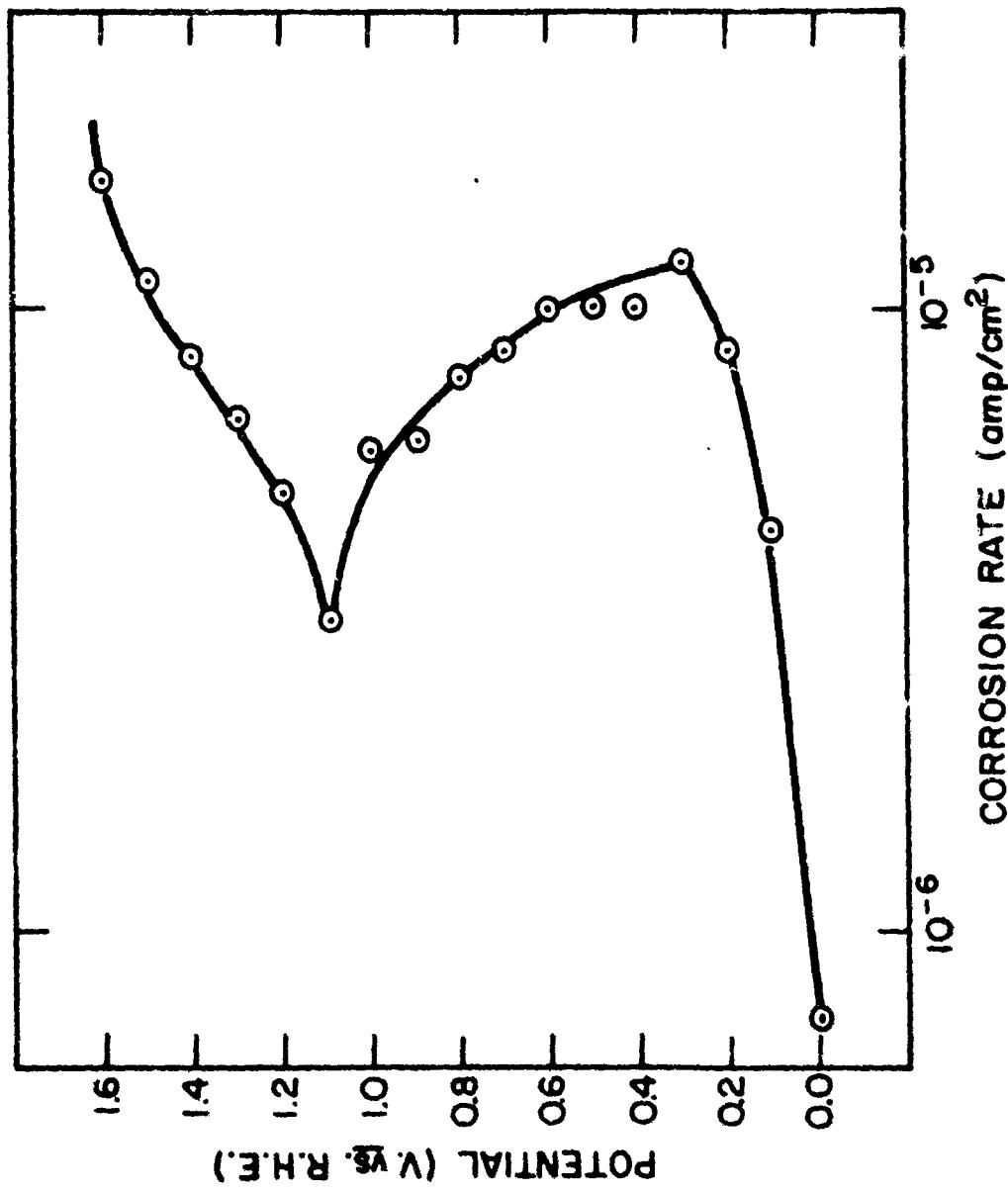
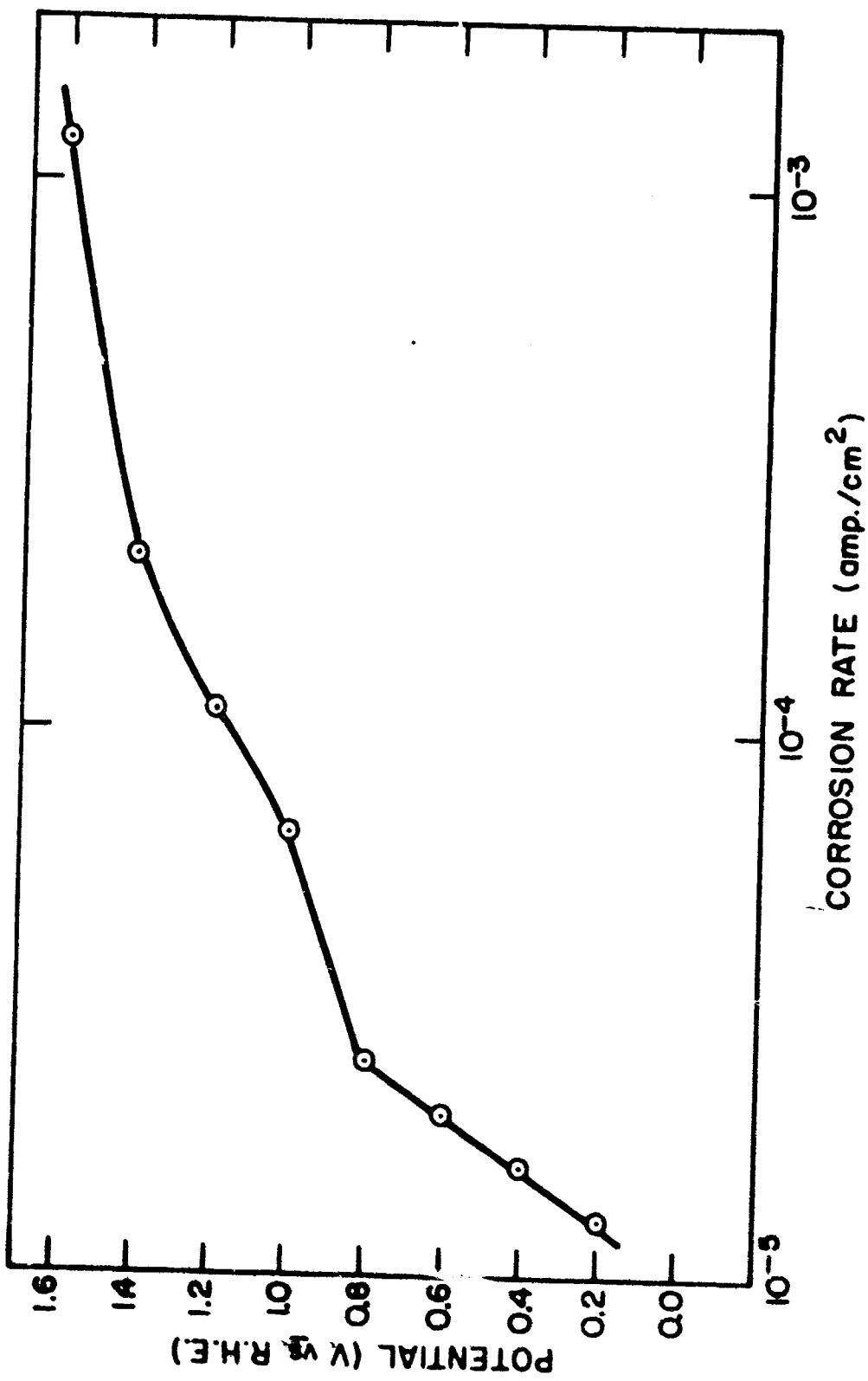


Fig. 6 Anodic dissolution of Mn in 1N KOH at 30°C, unstirred



potential arrest, suggesting the presence of a surface oxide. Below 0.6 v, the currents were much steadier but still quite low. The potential of the Mn returns to the  $H_2$ -evolution region on cathodic treatment and the metal behaves pretty much as before. The implication is that Mn would be suitable for alloying with Zn.

The corrosion of Co in KOH was also investigated. Since the currents were low and unsteady, it was not possible to obtain a meaningful current-potential curve. The electrode did not tarnish but the rest potential was very sensitive. Probably this potential was controlled by air films of Co oxides ( $\sim +0.25$  v) but when these had been reduced (after a few minutes at  $+0.3$  v), minor contamination with oxygen in the solution was able to control the potential at much higher values ( $+0.98$  v). Co appears promising for alloying with Zn.

The corrosion of Fe in KOH was investigated and the passive current was found to be very low, although erratic. Alloying with Fe will, therefore, be tried.

### 5. Corrosion of Zinc-Magnesium Alloys

Magnesium has good corrosion resistance in alkaline solutions (Fig. 2) and an alloy of 97 Zn - 3 Mg (wt %, not at % as in our previous reports) was therefore tested in KOH. Figure 7 compares curves in 1N KOH (stirred) for Zn and 97 Zn - 3 Mg.

The dissolution of the Zn-Mg is similar to Zn but about three times less. An important characteristic of the proposed system is not only the low passive corrosion rate but also the ready activation on demand. Zn in both 1N and 6N KOH readily activates either under cathodic galvanostatic driving or on open circuit. The cathodic chronopotentiogram thus taken has a delay corresponding principally to the reduction of dissolved zincate. To test the suitability or otherwise of the Zn-Mg system in this respect, we carried out the following experiment. The electrode was left at  $+1.2$  v, well into the

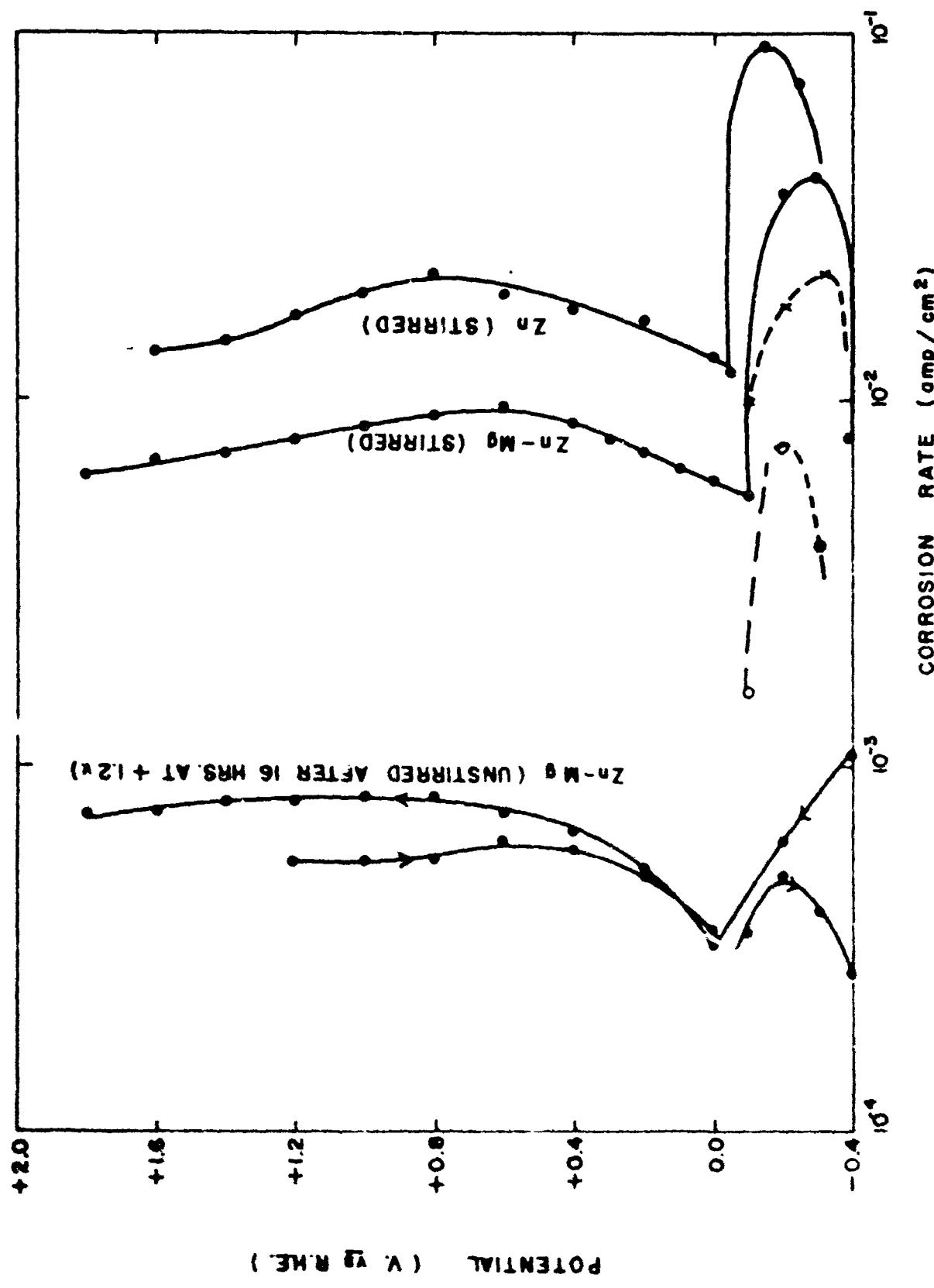


Fig. 7 Corrosion of Zn and 97 Zn - 3 Mg in N KOH at 30°C

passive region, without stirring (Fig. 7). During this time (~ 16 hours), the current fell from  $7.9 \text{ mA/cm}^2$  (stirred) to  $0.56 \text{ mA/cm}^2$  (unstirred). Then the oxidation rate of the electrode was studied as before and the electrode, which was black, was inactive as shown in Fig. 7. Although the open circuit potential was still in the zinc dissolution region (- 0.37 v) and was rapidly attained on breaking the circuit, it was not possible to activate this electrode again either by vigorous  $\text{H}_2$ -evolution (attempting to reduce the passive film) or by vigorous  $\text{O}_2$ -evolution (attempting to reach the transpassive region). In fact, the passive layer behaved like an ohmic film with a resistance (measured with a current interrupter) of about  $21.5 \text{ }\omega$ .

In a subsequent experiment the electrode was repolished and run through the active dissolution regime (unstirred) as shown in Fig. 8 (crosses). Then, we waited 45 min. at 0.1 v, which is the beginning of the passive region. During this time (5 min. to 15 min) the current fell from 10 to  $3.3 \text{ mA/cm}^2$ . The aim of this experiment was to investigate just where in the passive region the black ohmic layer is produced. Subsequently, the electrode was rather inactive (even after  $10 \text{ mA/cm}^2$  of  $\text{H}_2$ -evolution for 20 min.); for example, the maximum dissolution rate of the alloy was down to  $7.5 \text{ mA/cm}^2$  from  $22 \text{ mA/cm}^2$  (unstirred) and extended for a range of less than 0.1 v (in the vicinity of - 0.2 v vs. R. H. E.). Such a curve, taken in the active dissolution region of the alloy, is shown dotted in Fig. 7 (black circles). Repetition of this procedure lowered the maximum dissolution current to  $4 \text{ mA/cm}^2$ . From this experiment it appears that deactivation of Mg-Zn occurs even as low as - 0.1 v vs. R. H. E.

Reactivation of the alloy by cathodic galvanostatic pulses was attempted. Such activation is possible, although it did not remove the loose black material covering the surface. The possibility of zinc plating from solution onto the alloy electrode during the cathodic pulse was considered, and it was concluded that it did not affect the

results appreciably. Therefore, activation is not due to oxidation of Zn plated out from the solution during the cathodic "activation". We are sure of this because the extra charge due to active dissolution at say - 0.3 v is much larger than could be accounted for by plated zinc. For example, after one minute of a cathodic activation at - 1 mA, no more than 60 mcoul of Zn could be plated onto the electrode. (This assumes no  $H_2$ -evolution, there is some however.) This is then the maximum excess charge which could be attributed to plated zinc in subsequent oxidation of the alloy. In practice, we find at least 1200 mcoul (Fig. 8). Cathodization for longer times gives a more long-lived activation.

It is evident that we are partially reducing a very refractory surface layer which is forming at the active dissolution potential and that this cannot be the black and rather porous-looking layer which the electrode acquires after some time under active dissolution. Deactivation of the corrosion, both in the "active" dissolution potential region (Fig. 9) and in the subsequent "passive" region, evidently occurs, because of formation of a surface layer which is difficult to remove. Presumably, this is complicated by loss of zinc from the surface layers, but it is not certain that this is a predominant effect. The Mg-Zn solid solution system does not look very promising because the presence of Mg seems to limit the active dissolution of Zn rather more than it lowers the passive current.

Experiments with  $MgZn_2$  are planned since the compound should have quite different active-passive characteristics from the constituent elements. Also, although the loss of Zn from the surface layers may be a problem in the solid solutions, the compound is expected to be more coherent in this respect.

#### 6. Corrosion of Zinc-Copper Alloys

Cu has good corrosion resistance to 1N KOH (Fig. 3) and therefore its alloys with Zn were tested.

Figure 8  
Anodic Dissolution of 97.7n - 3 Mg in 6N KOH at 30°C, unstirred

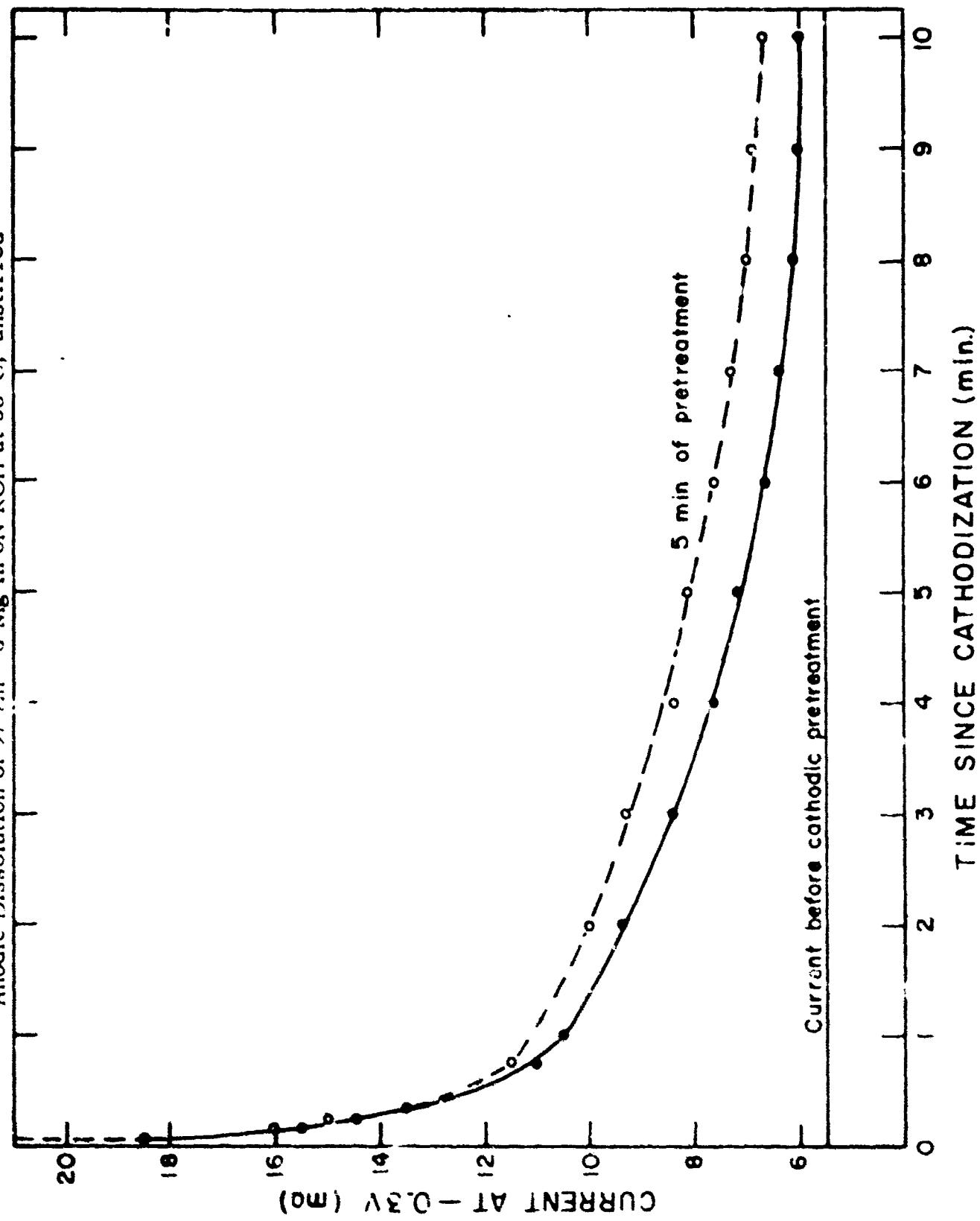


Figure 9  
Anodic Dissolution of 97 Zn - 3 Mg in 6N KOH at 30°C, unstirred

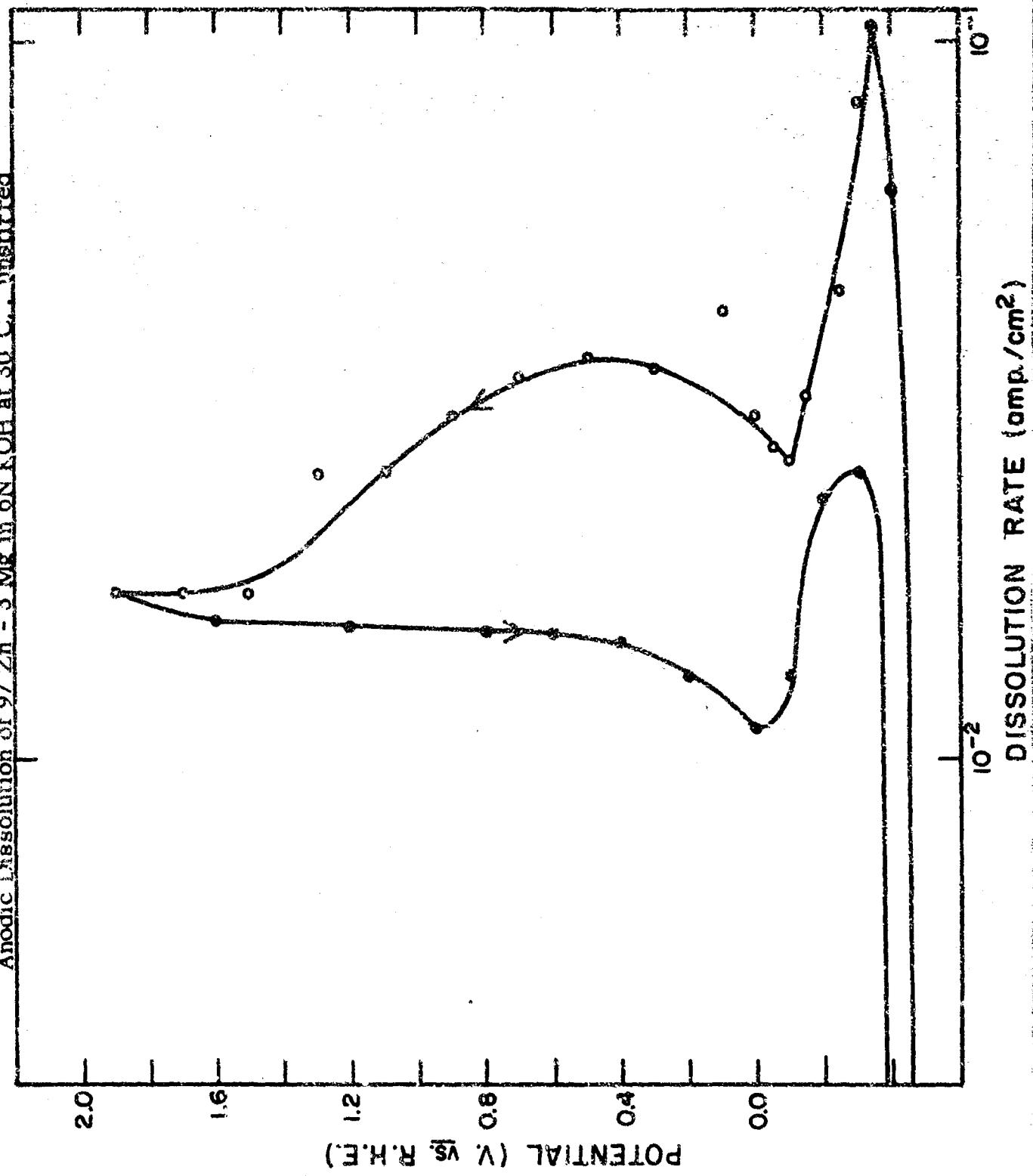


Fig. 10 shows the dissolution of 67-33 Zn in 1N KOH. The passive current is about ten times higher than that of Cu. After 17 hours at 1.2 v, this decreased to  $15 \mu\text{A}/\text{cm}^2$  and the electrode became black. The electrode was fairly readily activated but, as can be seen from Fig. 10, the over-all behavior does not show the Zn active dissolution region.

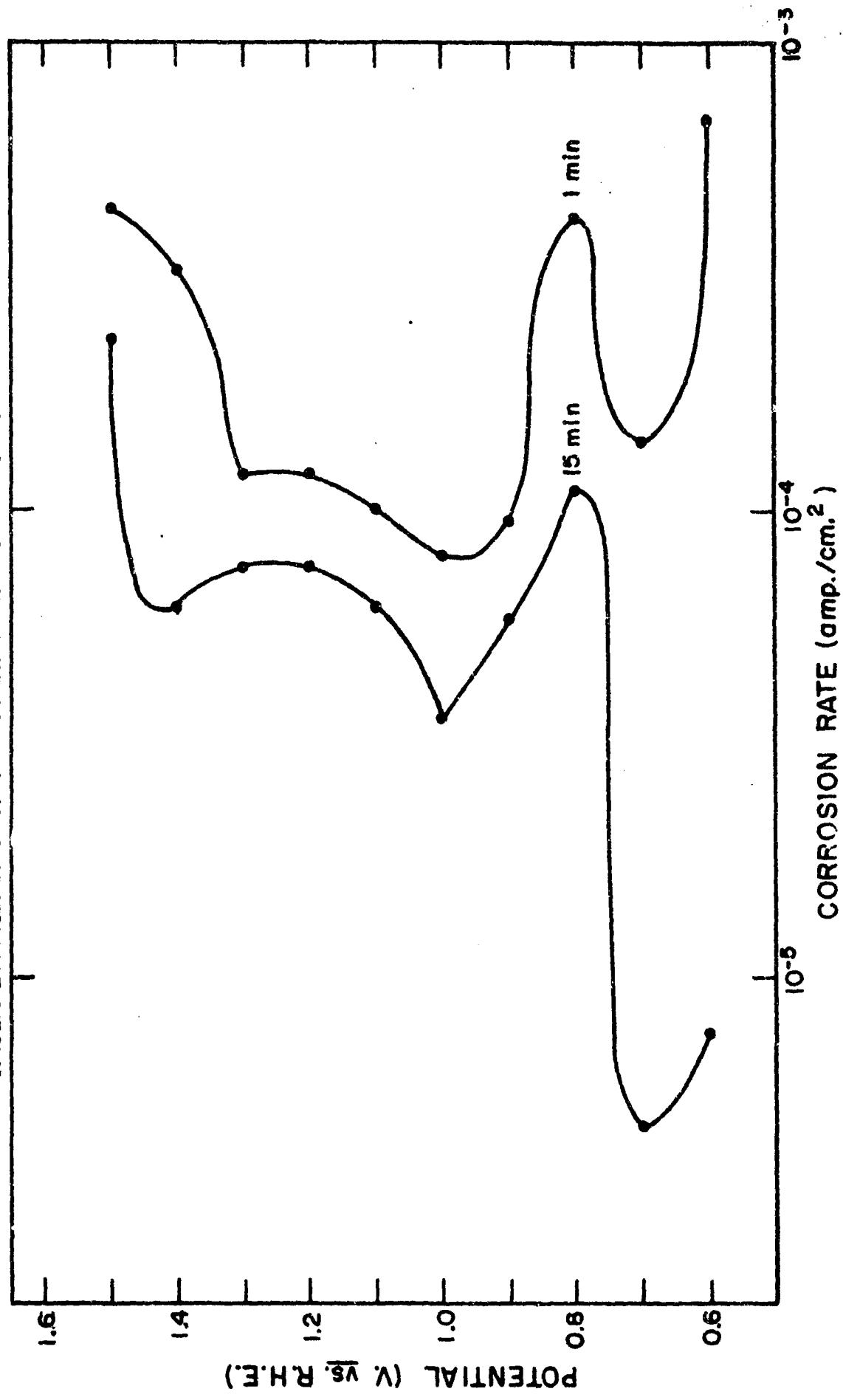
The corrosion of 80 Zn - 20 Cu (wt %) in 1N KOH is shown in Fig. 11. This curve shows currents taken point by point after 5 minutes at each potential. The currents were fairly steady; e.g. at - 0.2 v there is no change from 1 min to 5 min and between 0.5 and 0.7 v, the worst region, it decreased by < 50% in this time range. The diagram shows that the active dissolution of Zn has been pushed from  $\sim -0.3$  v to  $\sim 0.1$  v and that the critical current is  $\sim 10 \text{ mA}/\text{cm}^2$  (vs.  $\sim 60 \text{ mA}/\text{cm}^2$  for pure Zn at  $-0.3$  v. This undoubtedly reflects the lowering of Zn "activity" in the alloy. After the first passivation at  $\sim 0.3$  v, the electrode shows another active peak at 0.55 v and another at 0.85 v. Another peak is seen at 1.1 v. This complex corrosion behavior cannot be fully accounted for at this time and it appears inappropriate to investigate the system more fully in this context. The lowest passive current is at  $\sim 1.0$  v; this is  $1.7 \text{ mA}/\text{cm}^2$  after 5 min and still  $0.9 \text{ mA}/\text{cm}^2$  after 17 hours.

The conclusion from these studies is that Cu-Zn alloys do not have suitable corrosion properties for the primary reserve battery. This is because the effect of the added Cu is both to raise the active dissolution potential of the Zn and to decrease its critical current, not to lower its passive current enough.

As an alternative to alloying Cu with Zn, we considered briefly the possibility of protecting the Zn by plating Cu onto it. In this configuration the Zn electrode would be stored Cu-plated. Cu does not corrode at open circuit once  $\text{O}_2$  in this electrolyte has been consumed. To activate the battery a pulse is applied to dissolve Cu. One possible disadvantage of this procedure is that it could not

Figure 10

Anodic Dissolution of 67 Cu - 33 Zn in 1N KOH at 30°C. unstirred



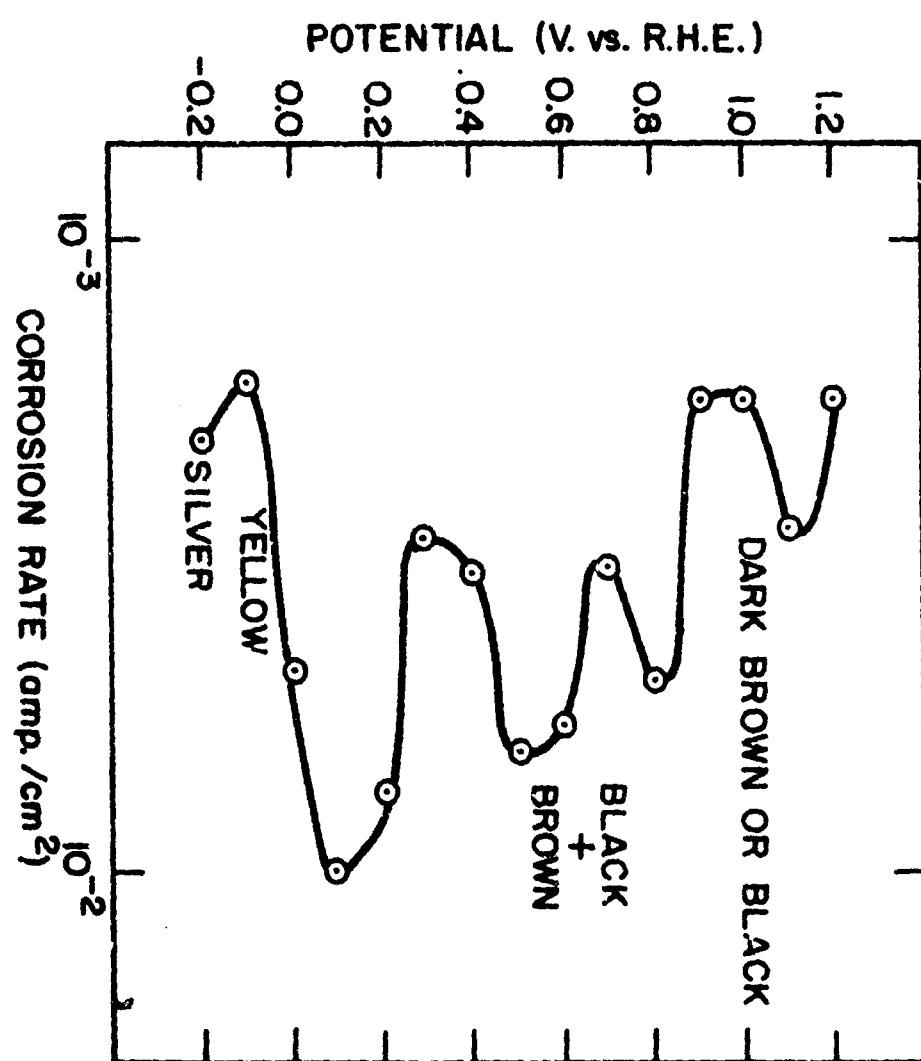


Fig. 11 Anodic dissolution of 80 Zn - 20 Cu in 1N KOH at 30°C, unstirred

be used for porous Zn (high rate) anodes, only for smooth ones. Another possible problem is that in order to protect the Zn we might have to put a large thickness of Cu onto the Zn (e.g. say microns). This would make activation difficult. Even worse, once the Cu had been removed during the activation procedure, it might plate back onto the Zn, which will now be well negative of the Cu reversible potential ( $\sim + 0.55$  v).

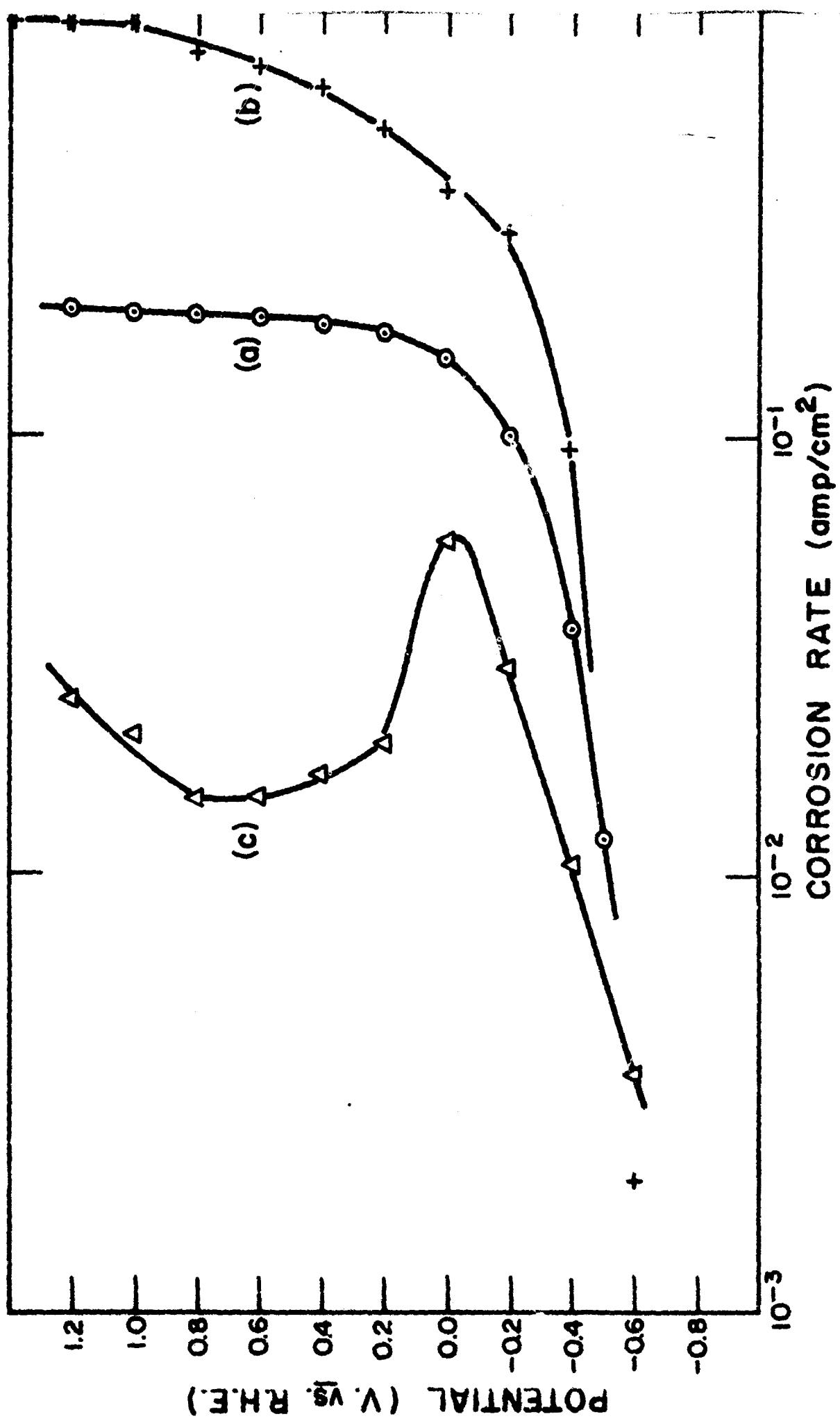
To test this notion, we attempted to plate Cu onto Zn. The minimum successful plate used so far involves about 1 coul/cm<sup>2</sup> from a cyanide bath and about 10 coul/cm<sup>2</sup> from an acid sulfate bath ( $\sim 6000$  Å in all). This amount of Cu on Zn gave the Cu potential in 6N KOH. However, although it can be removed by anodic discharge, activation is lengthy because of the large charge involved. Cu, once removed, will tend to plate back onto the Zn thus deactivating it. Thus, the activated Zn could only be used while dissolving very rapidly, e.g. - 0.2 v in 6N KOH. We conclude that further development will be necessary to make this procedure suitable for the complete protection of Zn anodes.

#### B. Corrosion of Mg

Mg has a very active dissolution potential (- 2.4 v vs. R.H.E. at pH = 0) and is a highly desirable anode material. Unfortunately, its performance is limited by a high open circuit corrosion rate, by rapid H<sub>2</sub>-evolution on discharge, and by rather higher open circuit potentials than one would expect (above - 1.2 v). If Mg could be used as an anode, one would achieve cells with very large potential and with very high energy density (equivalent weight of Mg is 12). We have sought to overcome one of the big problems of the Mg anode - its high open circuit corrosion rate, using the passive battery concept.

We have investigated the corrosion of Mg in a number of solutions where it might be used as an anode. In Fig. 12 we show the current-potential curves for Mg in these solutions. The results are somewhat approximate at the high current densities because of

Fig. 12 Anodic dissolution of Mg at 30°C. (a) 1N  $\text{NaClO}_4$  buffered to pH 7 with  $\text{NaH}_2\text{PO}_4$ ; (b) 1N  $\text{NaClO}_4$  unbuffered; (c) 0.2M  $\text{NaF}$  at pH 2 (using HF).



iR drops. These occur not only in the solution, between the working electrode and the tip of the Luggin capillary, but also in the layer of corrosion products which accumulate on the electrode. This latter makes automatic electronic iR compensation very difficult. The results are presented without correction and the errors are considerable since, for example at + 1.0 v vs. R.H.E.,  $H_2$  is still being rapidly evolved from the electrode. In all cases, thick white precipitates of corrosion products formed on the electrode. Despite these strictures, the curves in Fig. 12 are representative of what would actually be found for a battery anode.

Since the reversible potential of  $Mg^{+2}/Mg$  is - 2.4 v and the open circuit potential is typically -0.8 v, it is apparent that the open circuit potential is a mixed potential between the  $H^+/H_2$  reaction and the  $Mg/Mg^{+2}$  reaction. The major question is whether the intersection of the current-potential curves for these reactions occurs in the active part of the  $Mg/Mg^{+2}$  dissolution reaction or where the reaction is impeded by the formation of a passivating oxide. If the latter is true (as suggested by King for neutral and alkaline solutions, *J. Electrochem. Soc.*, 110, 1113 (1963)), the dissolution of a Mg anode must occur transpassively and the passive reserve configuration is not possible. According to Fig. 12 this is the case in pH7  $NaClO_4$  and pH7  $NaClO_4$ ,  $NaH_2PO_4$ . In the more acid  $F^-$  solution there is some evidence for active-passive transformation but it may reflect the accumulation of macroscopic amounts of  $MgF_2$  which block the surface, rather than the formation of a thin passivating film. Evidence for this was obtained with cathodic galvanostatic pulses from which it appeared that after a few minutes at 1.0 v vs. R.H.E., the ohmic drop was 40  $\omega$  and the double layer capacity was only  $\sim 15 \mu F/cm^2$  although the electrode was very badly etched. Further experiments to investigate the behavior of Mg in mildly acid solutions, where it does not form an insoluble product, are in progress.

Al shows the same phenomena in dilute acid solutions as does Mg. Thus, the open circuit potential is very high: current-potential curves similar to those in Fig. 12 are found, and as with Mg,  $H_2$  evolution increases as the potential increases (the "negative difference effect"). Studies on Al are not being continued at this time.

### III. CONCLUSIONS

Zn and Zn alloys show the appropriate current-potential characteristic in alkaline solutions for possible use in the passive reserve mode. Possible elements for alloying with Zn which appear to have appropriate passive currents are Co, Cu, Fe, Mg, Mn, and Ti. Alloys of Zn-Cu are not suitable, however, as the addition of Cu lowers the Zn critical current and does not lower the passive current enough. Zn-Mg solid solutions show the formation of an inactive surface layer and are not suitable. Cu plating of Zn may be suitable for its protection on standby.

Mg is in the passive state on open circuit in neutral and alkaline solutions. A secondary passivation may be found in mildly acid fluoride solutions.

#### **IV. FUTURE WORK**

Studies to confirm whether Mg shows a secondary passivation in acid solutions will be continued and possible alloying constituents to enhance any such passivation will be considered. Studies of Zn alloys - notably Zn-Fe, ZnMg<sub>2</sub>, Zn-Co, and Zn-Mn - will be continued.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and Indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION Unclassified
Tyco Laboratories, Inc., Waltham, Mass.		2b. GROUP
3. REPORT TITLE  Electrode Passivation Studies		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Second Quarterly Report - March 1 - May 31 1966		
5. AUTHOR(S) (Last name, first name, initial)  Brummer, S.B., Makrides, A.C. Bradspies, J.		
6. REPORT DATE May 31, 1966	7a. TOTAL NO. OF PAGES 32	7b. NO. OF REPS 0
8a. CONTRACT OR GRANT NO. AF 33(615)-3433	8b. ORIGINATOR'S REPORT NUMBER(S)	
8c. PROJECT NO.  c.  d.	8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. AVAILABILITY/LIMITATION NOTICES  Foreign announcement and dissemination of this report by DDC is not authorized.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Air Force Air Force Aero-Propulsion Lab. Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT  Studies of the passivation of Zn and Zn-alloys in KOH at 30°C have been made potentiostatically. Zinc shows the characteristic active-passive current-potential curve although the passive current is too high for use in the passive reserve mode in Zn-AgO batteries. Studies of the corrosion of Co, Cu, Fe, Mg, Mn, and Ti in alkaline solutions show them as possible choices for alloying with Zn to improve its standby characteristics. Cu-Zn alloys are not acceptable however, since the addition of Cu lowers the Zn critical current but does not lower the passive current sufficiently. Zn-Mg solid solutions show the formation of an inactive surface layer and are therefore not suitable. Cu-plating of Zn may be suitable for its protection on standby.		
Studies of the passivation of Mg from pH 2 to 14 were carried out with a view toward using the high energy density characteristics of the Mg-m-dinitrobenzene battery. In neutral and alkaline solutions Mg is passive on open circuit and cannot be used in the passive reserve mode. A secondary passivation may be present in mildly acid fluoride solutions.		

DD FORM 1 JAN 64 1473

Unclassified

Unclassified

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Primary Batteries						
Reserve Batteries						
Anode Passivation						
Zinc-Silver Batteries						
Zinc Alloy Corrosion in alkali						
Magnesium Anodes						
Magnesium Corrosion						
INSTRUCTIONS						
1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, sub-contractor, grantees, Department of Defense activity or other organization (corporate author) issuing the report.	imposed by security classification, using standard statements such as:					
2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.	(1) "Qualified requesters may obtain copies of this report from DDC."					
2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.	(2) "Foreign announcement and dissemination of this report by DDC is not authorized."					
3. REPORT TITLE: Enter the complete report title in all capital letters. This in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parentheses immediately following the title.	(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."					
4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.	(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."					
5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.	(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."					
6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.	If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.					
7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.	11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.					
7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.	12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.					
8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.	13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.					
8b. D. C. & M. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, sub-project number, system numbers, task number, etc.	It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (T), (S), (C), or (U).					
9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.	There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.					
9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).	14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content. The assignment of links, roles, and weights is optional.					
10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those						